ENEDIOLS FROM DURIL AND ISODURIL

BY

STANTON COIT KELTON, JR.

B.S., Harvard College, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE UNIVERSITY
OF ILLINOIS, 1941

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ACKNOWLEDGMENT

The author is grateful to Professor R. C. Fuson for his help in this investigation.

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INTRODUCTION

A comparison of the enediols related to mesitil [1] and 2,6-xylil [2] has shown that not only *ortho* but also *meta* and *para* substituents may affect the stability of the stilbenediols. The enediols from the isomeric octamethylbenzils, duril and isoduril, were prepared in order to study further the influence of *meta* and *para* substituents.

HISTORICAL

The investigation [3] of 2,2′,4,4′,6,6′-hexaalkylstilbenediols has shown that the size of the *ortho* groups is an important factor controlling the stability of these enediols. As the size of the alkyl substituent is increased by changing from methyl to ethyl and then to isopropyl groups, the ability of the enediols to resist oxidation is enhanced. Although most stilbenediols are readily oxidized, they are stable in an inert atmosphere and, in the absence of catalysts, show no tendency to rearrange to the isomeric benzoins. In contrast to the enediols related to benzoylformoin, reductone and ascorbic acid, all of which have a carbonyl group adjacent to the enediol group, the stilbenediols are not acidic.

THEORETICAL AND DISCUSSION OF RESULTS

The stability of the stilbenediols is apparently a manifestation of steric hindrance. The blocking effect of the *ortho* groups accounts for the diminished reactivity of the *trans* form in contrast to the *cis* isomer. *Ortho* substituents, furthermore, inhibit resonance in the stilbenediols by preventing the molecule from assuming a coplanar structure. As a result the hydroxyl-hydrogen atoms are less mobile than in an unsubstituted stilbenediol, and so the *ortho* substituted enediols do not ketonize spontaneously. Other examples [4] of the steric inhibition of resonance have been discussed.

The properties of the *cis* and *trans* enediols from isoduril, when compared with those of the duril enediols, show that methyl groups in the *para* position decrease the stability of the enediols. The influence of *meta* substituents is much less important.

EXPERIMENTAL

Duroyl and isoduroyl chloride were coupled by the action of a binary mixture of magnesium and magnesium iodide [5] to form, respectively, duril and isoduril. The *cis* enediol from duril was produced as a by-product of the coupling reaction. The *trans* enediols were formed in each case by reduction of the corresponding diketone in methanol using a platinum catalyst. In the isoduril series the *cis* enediol was produced when the reduction was carried out in a 10 per cent solution of acetic acid in methanol. Duroin was formed by ketonization of the *trans* enediol in methanolic hydrogen chloride solution. Isoduroin was formed, however, by a prolonged hydrogenation of isoduril in low-boiling petroleum ether. The four enediols and the two benzoins were acetylated by the action of acetic anhydride.

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VITA

The author was born in Wollaston, Massachusetts, on November 13, 1915. He attended the public schools of Wayne, Pennsylvania until 1933 and then entered Harvard College. He was granted the Bachelor of Science degree in 1937. Since that time he has attended the Graduate School of the University of Illinois and has served as a teaching assistant in inorganic chemistry.